Master's Thesis of Engineering

Tunable Plasmonic Color Printing by Focused Ion Beam Nanofabrication

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Abstract

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Plasmonic color, which is a kind of structural colors, can be generated through the resonant interactions between light and metallic nanostructures. The manufacturing process of plasmonic color nanostructures is also addressed as plasmonic color printing.

This thesis presents analysis over the color printing process on metallic thin film and metal nanocomposite material. The former structure is a kind of all-mental metamaterial manufactured by putting periodic nanocavities on silver thin film, during which the focused ion beam (FIB) milling process is involved. The desired colors can be printed on single silver film by tuning the nanocavity distance based on the principle of surface plasmon resonance.

The later structure is manufactured by duplicating the nano-patterns from silicon mold fabricated by FIB to the surface of a kind of stretchable optical material, which is manufactured by mixing silver nanoparticles and polydimethylsiloxane (PDMS) in the weight ratio of 1:100. Due to the possession of the properties of both substrate material PDMS and filling material Ag nanoparticles, this nanocomposite material presents both high elasticity and good plasmonic color effect based on the principle of localized surface plasmon resonance. The color of material surface will change with the geometry deformation of nanostructures due to the stretching of the patterned nanocomposite material. A shape memory composite (SMC) actuator with nanopatterns on the surface was manufactured to illustrate how this printing technology is going to be applied in color based strain sensors.

With the strengths of easy fabrication and large color tuning range, this design can be used in sensor applications and the future plasmonic color display technology.

Keyword: Tunable plasmonic color, Nanofabrication, Focused ion beam, Nanocomposite.

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Chapter 1. Introduction

1.1. Study Background

1.1.1 Structural color printing

There are there kinds of colors in the nature world: pigments, structural colors and bioluminescence [1]. Within them, structural color is a kind of coloration generating from regularly arranged nanostructures with the scale less or comparable to optical wavelength. Different optical interactions including multilayer interference, scattering, diffraction grating, photonic crystal, and combinations result in selective transmission or reflection of particular light wavelengths, which leads to the generation of structural colors [2].

Recently, with the development of micro and nano scale fabrication technology, artificial structural coloration has attracted scientific interest as structural colors perform properties of never fading, high resolution, easy tunability and supernormal optical properties. Especially in the field of non-contact sensor, color filter and information storage, structural coloration plays an important role in next-generation technology revolution [3~4]. The artificial structural coloration, including diffraction optic device, photonic crystal, and plasmonic structure can be fabricated by up-to-down or down-to-up manufacturing such as thin film deposition, lithography etching, nano-imprinting, colloidal self-assembly, electrochemical corrosion for different manufacturing material and objectives [5~8].

The structural color printing process, in other words the nanofabrication process of periodic nano-structure, need to be process simplified, material saving and what's more important, realize the continuous and precious color tuning. The tunability of structural color, in fact has two categories: passive color tunability and active color tunability. The passive color tunability can be realized by changing the size and geometry of periodic structure, adjusting the structure period or external conditions like surrounding medium, light source and so on.

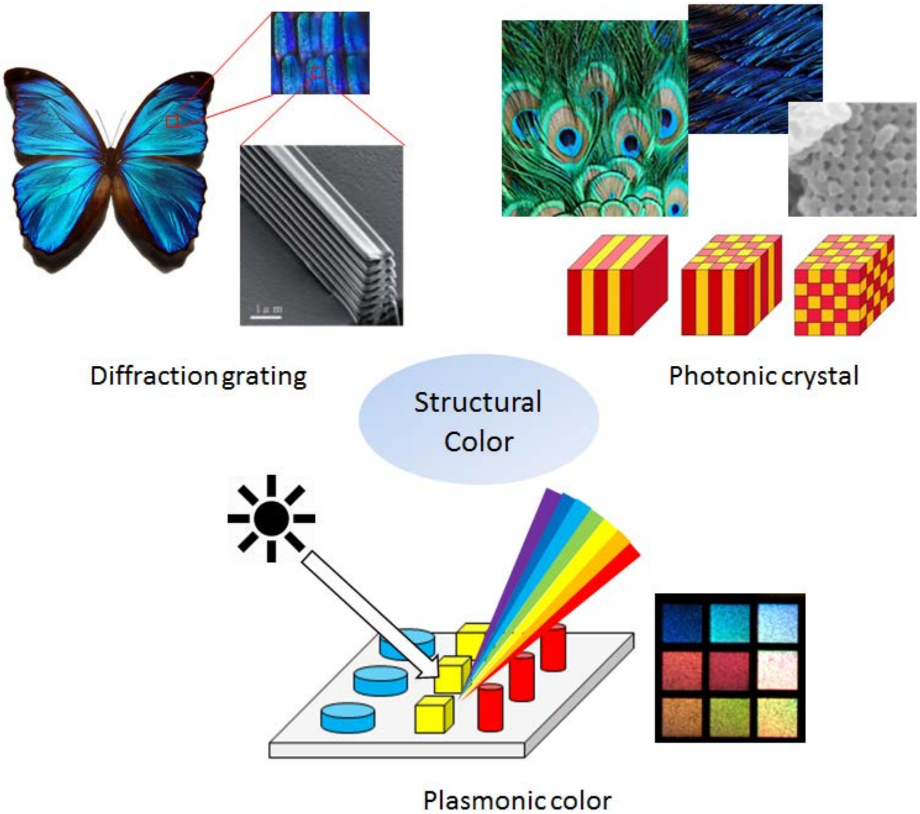


Figure 1.1 Main types of natural and artificial structural colors

Figure 1.2 High color resolution of structural colors compared with traditional color printing color display technology

On the other hand, active tunable structural colors, with the properties of deformable without breaking period structures, can show color change with the active change of nanostructure geometries [9].

1.1.2. Plasmonic color

Plasmonic color is a kind of structural color generated from the resonant reactions between incident light and metallic nanostructures. Under the illumination of visible light, noble metal materials can perform surface plasmon resonance, coupled with the strong interaction between metallic nanostructures and incident light [10]. Plasmonic colors can be generated in the form of reflective colors or transmissive colors at the metallic and dielectric material interface.

Different with traditional structural colors, plasmonic colors arise due to the localized resonances of metallic nanostructures instead of diffractive effects. With the development of nanofabrication technology, it becomes possible to fabrication subwavelength nanostructure to generate plasmonic colors which can beat diffraction color limit in nature world. Color printing with plasmonic structure, performing high resolution, high efficiency and color tunability, open a new way to generate and manipulate color in nanoscale. By changing the geometry and dimension of nanostructures, the intensity, phase and polarization of scattering light can be manipulated based on the principle of surface plasmon resonance. Plasmonic colors are also related with incident angle, viewing angle and the refractive index of surrounding environment [2]. In the near future, plasmonic color is a promising technology in the application filed of optical data storage, color imagining and biosensors.

1.1.3. Focused ion beam nanofabrication

Focused ion beam (FIB) is widely used in manufacturing complicated micro/nanostructures for different applications. In comparison with other micro/nano manufacturing technologies, FIB nanofabrication has specific strengths such as high resolution, high flexibility, maskless processing and rapid prototyping [11]. FIB system in fact is an integrated platform combining an ion beam machining tool with the resolution of tens nanometers and a microscope with nanometer's imaging resolution [12]. Versatile materials, especially metal materials with good electric conductivity, can be machined by FIB system effectively in high resolution up to tens of nanometers.

The research of plasmonic color need to study the interaction of metallic nanostructures and light, complicated nanostructure with flexible design and nanoscale resolution is required in experiment process. In this point, FIB is an ideal manufacturing tool for plasmonic colors.

1.2. Purpose of Research

In this research, our objective is to manufacture both passive and active tunable plasmonic color by FIB nanofabrication. Passive tunable plasmonic color will be printed on metal thin film by FIB milling process. The FIB fabrication condition of plasmonic nanocavity structures, the relation between cavity distance and reflected colors will be studied and complicated artworks with high resolution, vivid iridescence color will be manufactured. For the active tunable color printing, we aimed to develop a stretchable optical material with plasmonic colors on its surface and the colors can be changed by the deformation of the material itself. The color printing will be realized by replicating nanopatterns from FIB patterned silicon wafer to material surface. Further application like color based strain sensor will also be demonstrated by this active tunable plasmonic structure.

Chapter 2. Color Printing on Metal Thin Film

2.1. Overview

Surface plasmons and related plasmonic nanostructure are the fundamental of plasmonic color printing on metal material. Surface plasmons are essentially collective oscillation of conduction electrons on the metal and dielectric material interface. In previous research, various metallic nanostructures such as nanodisks, nanoantennas, metallic gratings, metal-insulator-metal (MIM) nanoresonantors have been introduced [3]. Different with the color effect of pigments, which is determined by molecule energy level transitions, the reflection and transmission of light in plasmonic nanostructure are determined by their geometry and dimensions. Leveraging on the development of nanofabrication technologies, it becomes possible to control the shape and size of metallic nanostructure in tens of nanometer's precision. By adjusting the geometries of the plasmonic nanostructures, we can manipulate light properties, including visible-light wavelength selection and thereby generate structural colors [2].

In this research, a plasmonic structure manufactured by milling nanocavities with different distance on metal thin film will be introduced. The thin film was deposited on silicon wafer by electron beam physical vapor deposition (EBPVD) and then patterned by FIB with nanocavities in the same size and different distances. The two dimensional nanocavities can be seen as one dimensional grating structure when the incident light illuminates at one direction. Thus the plasmonic color effect of this structure can be explained by the grating coupled surface plasmon resonance (SPR) theory. Desired plasmonic colors can be manufactured by changing the nanocavity distance.

2.2. Principles

1.2.1. Surface plasmon resonance

Surface plasmon resonance is a charge-density oscillation at the interface of two media with negative and positive permittivity, for instance, metal and air. The charge density oscillations and associated electromagnetic fields are called surface plasmon-polariton waves.

Figure 2.1 shows the electromagnetic field intensity on the distance away from the interface, the electromagnetic field vectors reach their maxima at the interface and decay evanescently into both media. These waves can be excited very efficiently with light in the visible range of the electromagnetic spectrum [13]. The surface plasma wave (SPW) at the interface is a TM-polarized wave, which means that the magnetic vector is perpendicular to the direction of SPW propagation and parallel to the interface plane). The frequency-dependent surface plasmon wave vector k_{sp} can be expressed as

$$k_{sp} = k_0 \sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}} \tag{1}$$

where k_0 denotes the free space wave number, ε_m is the dielectric constant of the metal ($\varepsilon_m = \varepsilon_{mr} + i\varepsilon_{mi}$), and ε_d is the dielectric constant of the surrounding medium. According to the Eq. (1), k_{sp} is meaningful only when $\varepsilon_m + \varepsilon_d > 0$, that's to say, SPW may be supported by the structure providing that $\varepsilon_{mr} < -\varepsilon_d$. Within visible wavelengths, this condition can be satisfied by several metals of which gold and silver are the most commonly used [14].

At the interface of metal and dielectric material, if the incident light of specific spectrum resonances with the surface plasmon wave, the energy will transfer from photons to surface plasmon and then be absorbed by the surface plasmon wave. As a result, the intensity of reflected light with specific wavelength will decrease drastically. In the reflection spectrum, an obvious wave drop is the sign of surface plasmon resonance and therefore at the surface of metal material, specific reflected colors can be observed.

1.2.2. Grating coupling of surface plasmon resonance

The interaction between the surface charge density and the electromagnetic field results in the momentum of the surface plasmon mode k_{sp}, being greater than that of a free-space photon k_0 of the same frequency ω as shown in Fig 2.2 (a), the resulting momentum mismatch between light and SPs of the same frequency must be overcome if we want use light to generate surface plasmons [15].

Incident radiation at an angle θ with respect to the normal plane of metal surface can be scattered by the grating structure, at different diffraction orders, the wave vector of reflected radiation is increased or decreased by integer multiples of the grating wave vector k_g ($k_g = 2\pi/\lambda_g$). When a diffracted order has a wave vector can be coupled with the wave vector of surface plasmon in interface direction, it will not propagate and will become evanescent. As shown in Fig.2.2 (b), scattered dispersion curves (red line) that fall between the light lines (blue area) can be coupled.

The grating coupling condition between reflected radiation and surface plasmon wave is

$$k_{SP} = n_d k_0 \sin\theta \pm N k_g \qquad (2)$$

where $n_d = \sqrt{\varepsilon_d}$ is the refractive index of dielectric material, N is an integer and n is the refractive index of dielectric medium [16]. The reflected light wave and surface plasmon wave will resonate with each other and generate surface plasmon polarizations. The intensity of reflected light at corresponding wavelength will decrease drastically, consequently, the plasmonic colors generate at grating structure surface.

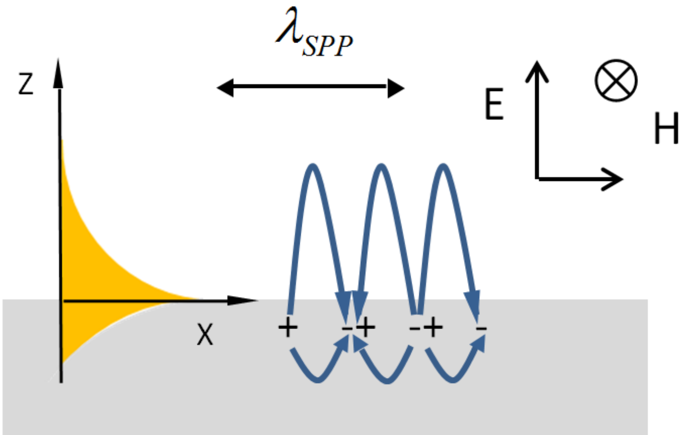


Figure 2.1 Surface plasmon polariton waves on metal–air interface

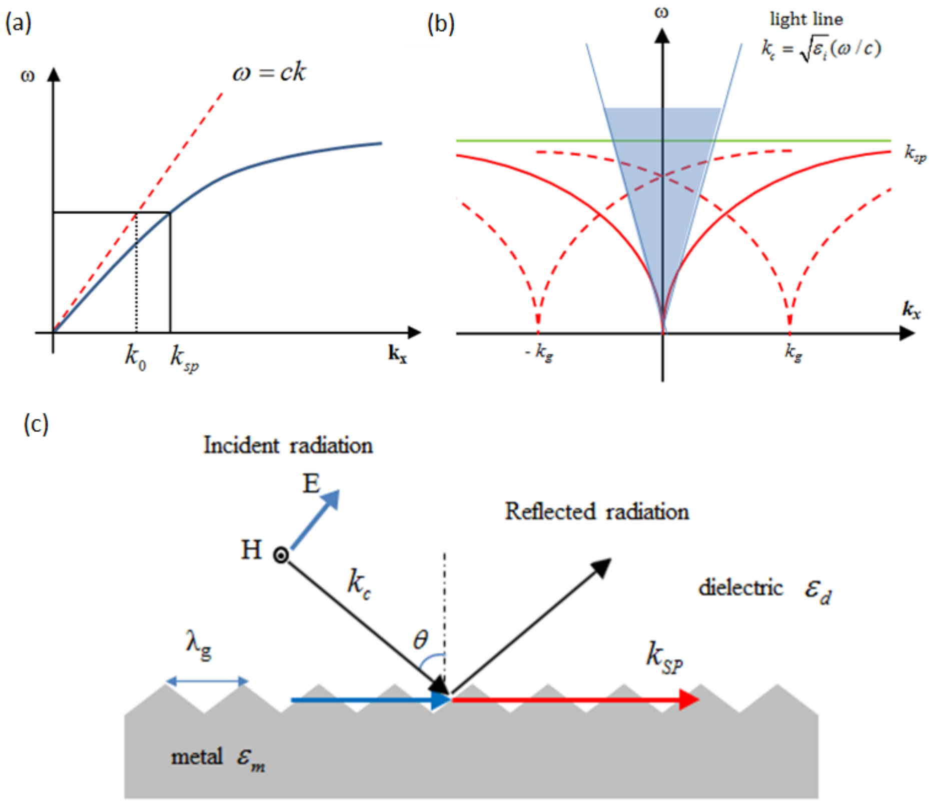


Figure 2.2(a) Dispersion cure of surface plasmon mode and incident light. (b) Dispersion curve of grating coupling of surface plasmon resonance. (c) Schematic of surface plasmon resonance coupling on metal and dielectric material interface

2.3. Design and manufacturing

Silver is the one of the most widely used metal material for plasmonic nanostructure manufacturing. In order to get smooth and plat surface for nanocavity pattering, we deposit silver thin film on silicon wafer. Firstly, silicon wafer was cleaned by ethanol and then DI water ultrasonic bath, finally dried by nitrogen gas gun. The silver film was deposited by electron-beam physical vapor deposition (PECVD) device at a deposition rate of 0.5nm/s to ensure the compactness and uniformity of film. The deposition thickness of silver film was chosen to be 150 nm as the silver film has to be thick than FIB patterned cavity depth to assure the reflection effect. The patterning process was finished by the FIB milling fabrication, after trying different milling conditions, the beam current we chose for patterning on silver film is 140 pA, dwell time is 0.01 ms and number of scan is 1000 times in the consideration of milling time, machining precision and reflective color effect. The size of milling cavities were measured by FIB imaging, the diameter R of upper hole is approximately 110nm and the depth of cavity structure is about 100 nm.

Keep the FIB milling condition the same and change the dotting distance of ion beam, we can get patterns with the same cavity size and different cavity distance. In FIB milling process, different beam current can be chosen to manufacture nanostructures under different precision demand. The higher the beam current is, the larger the milling spot size will be and consequently the milling time will be shorter. Even though FIB milling can manufacture nanostructure in tens of nanometer theoretically, taking into consideration of milling time and manufacturing cost, we decided to use ion beam with beam current of 170 pA in our experiment.

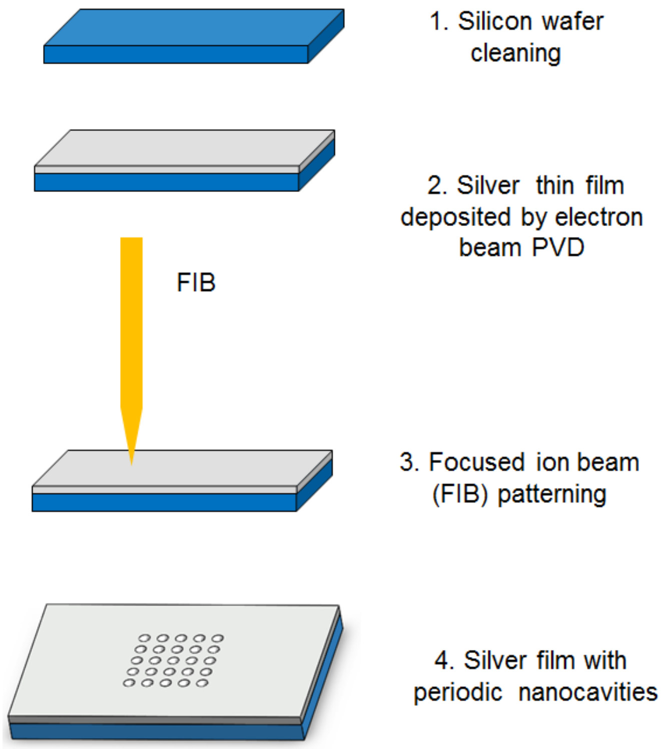


Figure 2.3 Manufacturing process of nanocavities on slilver film

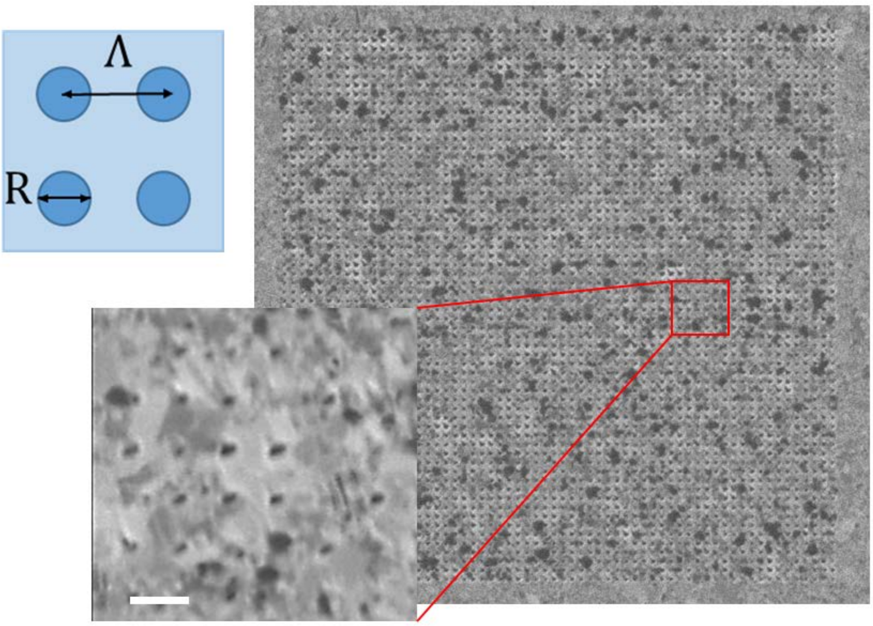
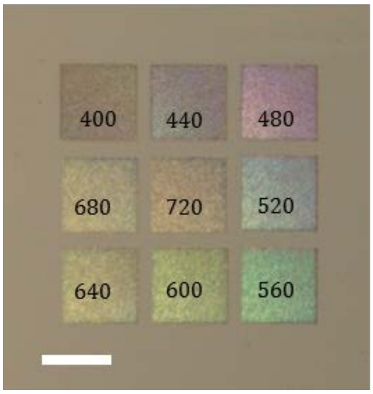


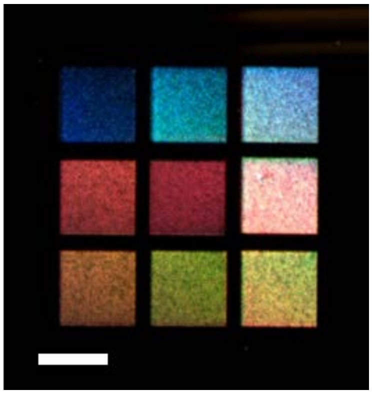
Figure 2.4 FIB imagine of patterned thin film (scale bar: 500 nm, Λ: c avity center distance, R: cavity diameter)

Plasmonic color can be generated by metallic nanostructures in subwavelength scale, subwavelength periodic structure can also scatter and diffract light beam into different directions with high energy efficiency. In order to generate plasmonic colors with high purity and brightness, we set the dotting distances range from 400nm to 800nm. By changing the cavity distance, the reflection color of silver film can be tuned continuously and precisely. To observe the color tuning process intuitively, nanocavities with different center distance was patterned on the same silver film as shown in Fig.2.5 (a). Under illumination of white light with 60° incident angle, by tuning cavity distance from 400 nm to 720 nm in step of 40nm, the observed reflection color at normal direction show color shift from blue to red, which covers the entire visible spectrum.

Under the same illumination condition and observation angle, reflected plasmonic colors and nanocavity distances perform corresponding relationship as shown in Tab.2.1. If put the nanocavities with different distances in specific sequences and areas, those nanostructures can work as color pixels in image displaying. With the assistance of bit-map function in FIB system, we designed and draw some art works as shown in Fig.2.6 on the same silver film to show the structural color diversity and the high resolution of plasmonic color up to subwavelength scale. The incident light here is 100W halogen white light source with incident angle of 60°. The fluorescence spectrum of those plasmonic colors was measured by the micro-spectrum test system which will be introduced in next section, the measured spectrum shows the color purity and tunability of printed plasmonic colors.



(a)



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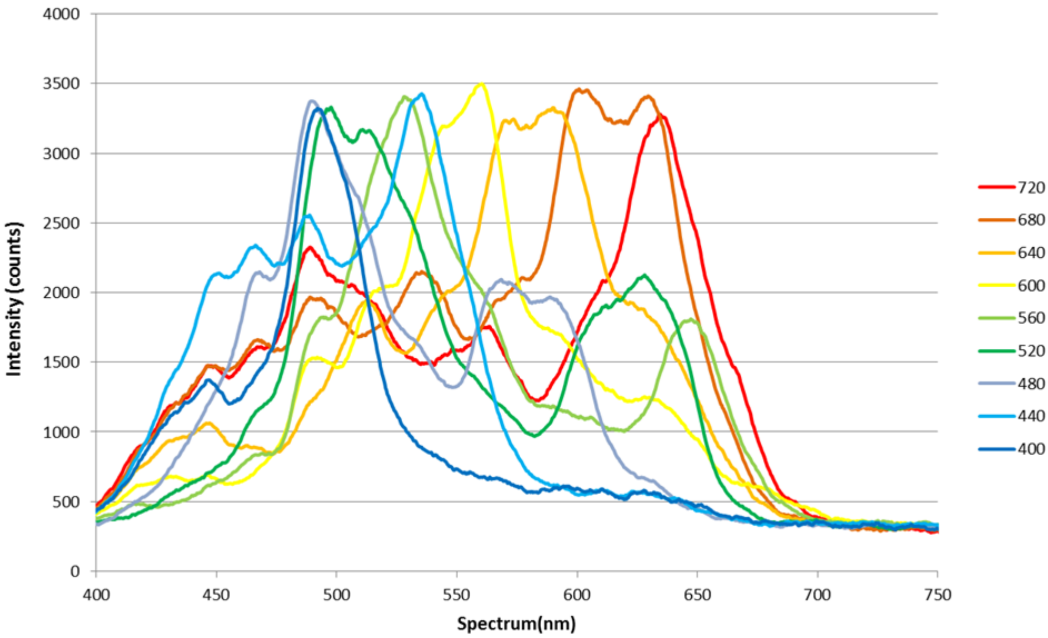

(c)

Figure 2.5 (a) Microscope image with normal incident light, the number in color block stands for center distance of nanocavities, number unit is nanometer, and scale bar is 30 μm. (b) Microscope image of the same sample with 60°incident light, scale bar is 30 μm. (c) Fluorescence spectrum of the sample under condition of (b).

Table 2.1 Relationship between cavity distance and reflection colors

Nanocavity Distance (nm)	Central wavelength (µm)	Color
400	498	
440	505	
480	510	
520	517	
560	525	
600	556	
640	584	
680	620	
720	642	

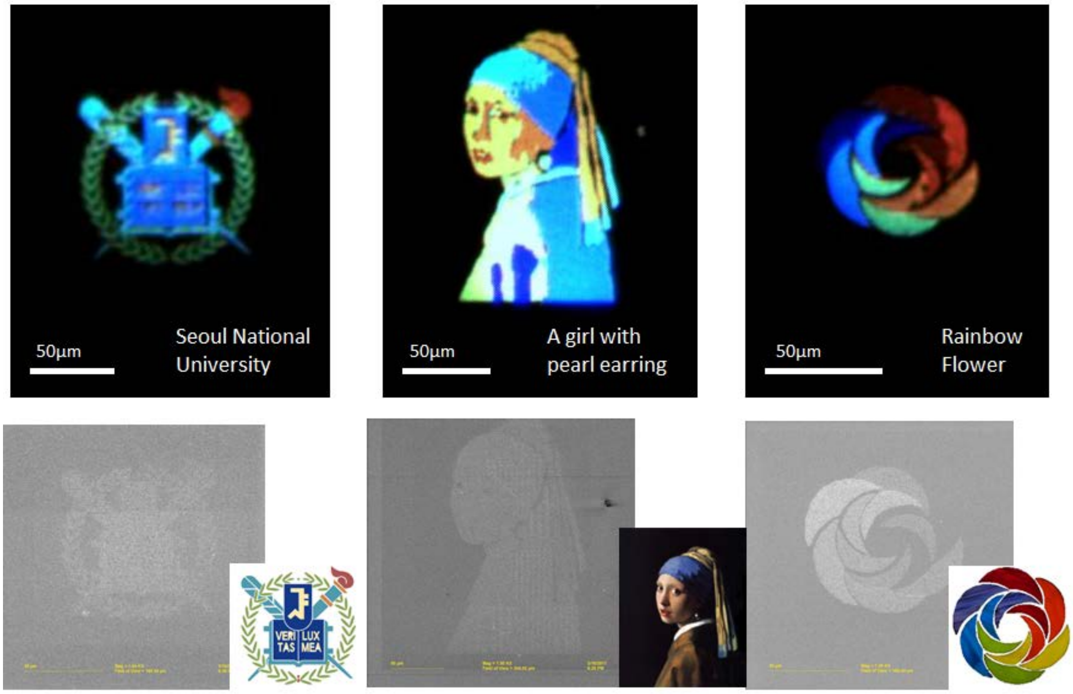

Figure 2.6 Dark background microscope images, FIB images and original designs of plasmonic color artworks on silver thin film

2.4. Measurement and evaluation

The measurement system of our experiment is composed of a fluorescence microscope (Olympus BX53), a miniature spectrometer (Ocean Optics flame spectrometer), a halogen light source (Philips 12 V 100 W), optical fiber, charge-coupled device (CCD) camera and etc. The outer light source can afford incident light with specific incident angle to excite the surface plasmon on metal surface with plasmonic nanostructure, on which the coloration effect can be observed by microscope at normal incident angle. We use normal halogen light source without polarization filter. Even though only P-polarized light will affect the surface plasmon resonance, as we test fluoresce intensity, not the reflective efficiency or the numerical index of reflected light, the polarization states of incident light source do not play an important role in color display. CCD camera can collect and transfer the optical information into computer image simultaneously.

The spectrometer connected into the microscope light path by optical fiber and C-mount adaptor can measure the reflected spectrum at micrometer scale with high efficiency and sensitivity, the measure area can be calculated by fiber diameter dividing microscope lens magnification factor. The optical fiber we using is 100 μm VIS/NIR fiber, the lens used for micro-spectrum measurement is X10 objective lens, therefor the measurement region of the micro-spectrometer is a φ10 μm circular area, which is small enough for FIB patterned plasmonic color measurement. .

Making use of this measurement system, plasmonic colors generated in microscale can be observed visually and measured numerically. By tuning the nanocavity distance, continuous and smooth color shift was realized. Based on the corresponding relation between cavity distance and reflection color, complicated colorful patterns was printed on silver film in high resolution and with clear boundary.

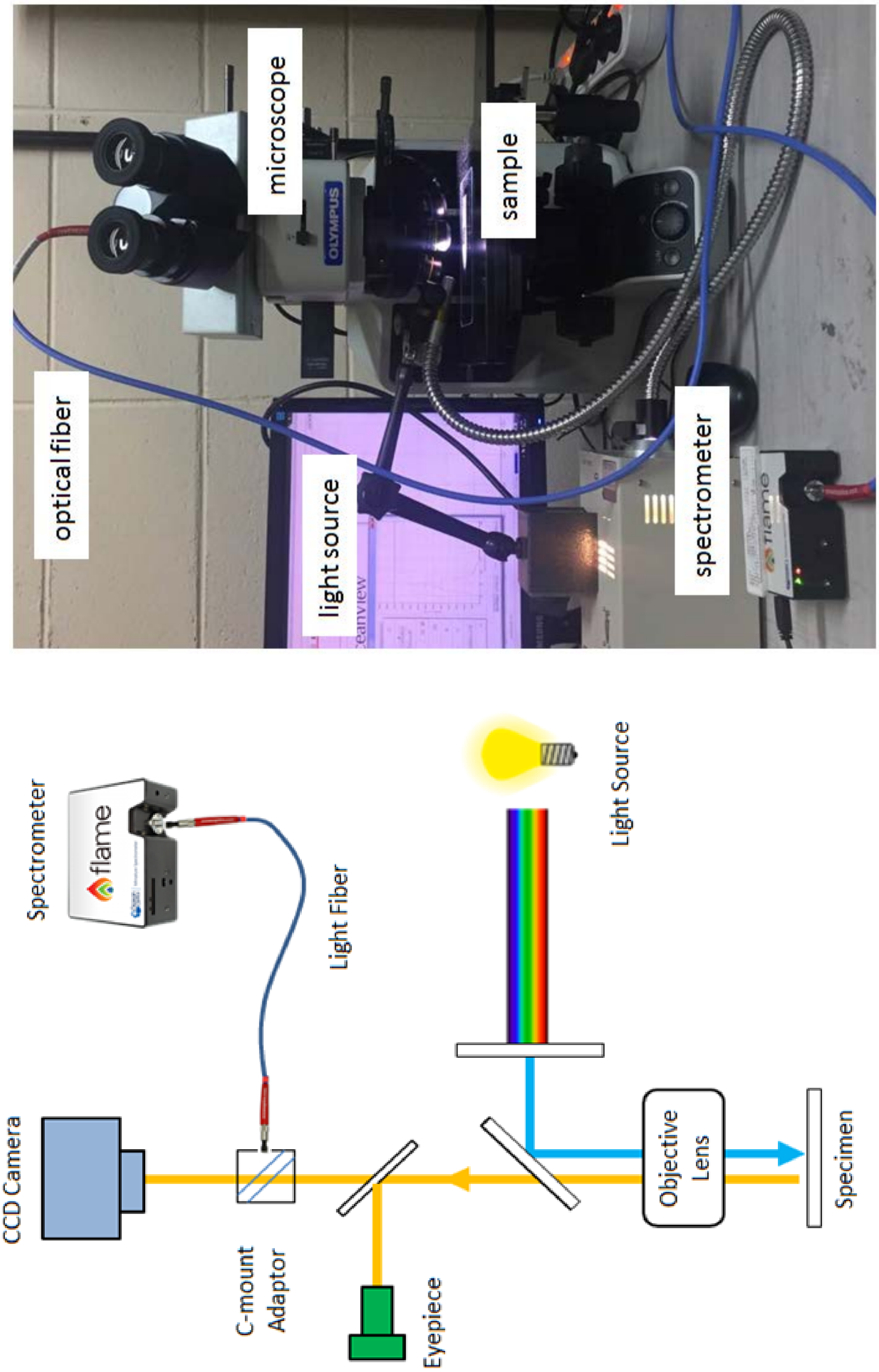

Figure 2.7 Color test and micro-spectrum measurement system

2.5. Summary

In this research, vivid plasmonic colors and complicated colorful patterns was manufactured by FIB nanofabrication on a single silver thin film. The nanocavity structures arrayed with different distance play the role of grating coupler which can couple the incident light wave with the surface plasmon at the metal-air interface, incident light with specific spectrum will be absorbed in metal in the form of surface plasmon resonance, then the residual lights will be reflected and show plasmonic coloration.

FIB nanofabrication process is flexible and convenient, what's more important, complex design of pattern in microscale and precision machining in nanoscale is possible. In our research, periodic nanocavity structures was manufactured directly only by single metal material—sliver and single manufacturing process—FIB milling, the time costed in patterning a 100μm square area is about 30 minutes. Comparing with the plasmonic color printing methods in previous research such as metallic nanorod arrays [17], plasmonic nanoparticles [18], the color printing method we use in this research show great design flexibility, process convenience and time efficiency. And because of the excellent oxidation resistance of silver, the printed plasmonic colors can last a long time in nature environment.

In order to evaluate the coloration effect, a micro-spectrum test system was set up to measure the fluorescence spectrum of microscale patterns. By changing the nanocavity distance, the reflected plasmonic colors can be tuned continuously and precisely. Complicated colorful patterns were printed on silver film to show the color quality and imaging resolution of this plasmonic color printing technology.

Chapter 3. Color Printing on Metallic Nanocomposite

3.1. Overview

In the nature world, organisms like chameleon can change the microstructure in their biological structure to generate tunable colors for camouflage and communication. There are intensive researches about those color change biological structures include expansion and compression if extracellular space between protein platelets in cephalopods, tilting protein platelet in the iridophore of neon tetra fish and changing refractive index of a porous layer by absorbing liquid onto the beetle shell. We can conclude that those structural color tuning mechanisms has three main factors: refractive index, periodic nanostructure and incident light angle [1].

In order to manufacture artificial active tunable structural colorations, researches have developed various methods such as stretchable opal composites by depositing an array of colloidal particles on a rubber sheet [19], flexible photonic metastructures by embedding silicon metastructures in a flexible membrane [20]. Most of them are focused on changing nanostructure attached on or embedded in soft materials such as polydimethylsiloxane (PDMS). In this research, we developed a new method by manufacturing periodic nanopillars on the surface of Ag-PDMS nanocomposite material to generate plasmonic colors. Instead of combining nanostructures and soft material together, nanopillars were manufactured by a single nanocomposite material through nanopattern transfer process. As the Ag-NPDS nanocomposite material performs both good optical reflectivity and mechanical elasticity, the periodicity of nanostructures on it can be changed with material deformation, there for the reflective plasmonic color on material surface can be tuned actively by outer forces which induce the material deformation. Tunable plasmonic color printing can be realized on metallic nanocomposite material.

3.2. Material

The key factor in fabrication of tunable plasmonic nanostructure with large deformation is the manufacturing of optical elastomer material with both excellent optical and mechanical properties [21~22]. Nanocomposite material can perform properties of both continuous phase and dispersion phase material; therefore, composite nanoparticles with excellent optical properties and elastomer materials with high elasticity can get the ideal material suitable for active tunable structural colors manufacturing.

By combining silver nanoparticles and PDMS at a specific ratio, linear and no-linear optical properties of PDMS material will change a lot. In that process, localized surface plasmon resonance (LSPR) effect of Ag nanoparticles play an important role. LSPR is an optical phenomena generated by a light wave trapped within conductive nanoparticles smaller than the wavelength of visible light [23].The phenomenon is a result of the interactions between the incident light and surface electrons in a conduction band. Noble metals such as Ag and Au are often used in optical devices as their energy levels of d–d transitions exhibit LSPR in the visible range of the spectrum. Nanoparticles undergoing LSPR can have high molar extinction coefficients for absorption, and Mie scattering that can be many orders of magnitude larger than without LSPR [24~25].

In order to manufacture reflective elastomer material, in our experiment, we chose 100 nm Ag nanoparticle as dispersion phase material, PDMS as continuous phase material to manufacture Ag-

PDMS nanocomposite material. We tested the reflection effect and mechanical strength of nanocomposites at different Ag nanoparticle fill factor, finally the nanocomposite was decided to make by mixing 0.2 g Ag nanoparticles and 20 g PDMS liquid precursor (Sylgard 184 Silicone Elastomer Kit from Dow Corning, mixed in a 10:1 ratio) The weight ratio of Ag and PDMS is 1:100, the volume fraction of Ag is calculated to be 0.001. After mixing Ag nanoparticle and liquid PDMS uniformly by stirrer, the composite was kept in 100℃ environment for 30 minutes to finish curing.

The reflection spectrum of the manufactured Ag-PDMS composite was measured and the results show that the composite material show reflectance of around 10% in visible spectrum. The elasticity was tested by stretching test; the manufactured nanocomposite elastomer with thickness of 2 mm can be stretched up to 50% linear deformation without breakage.

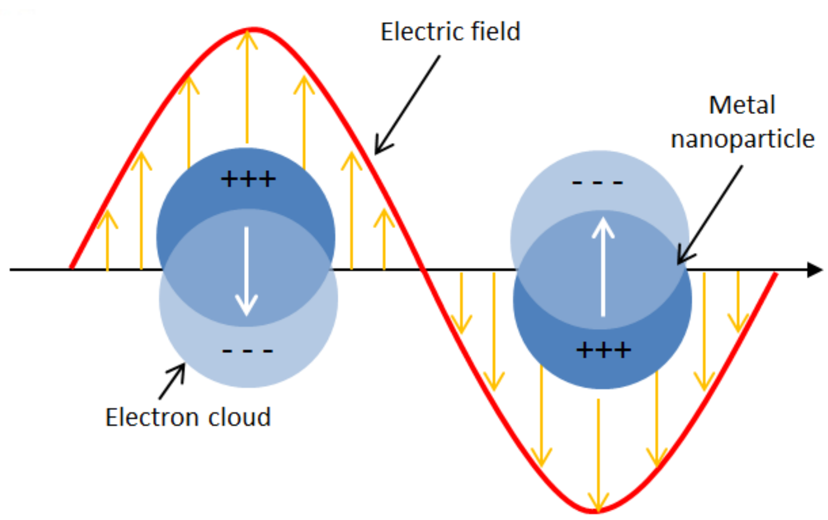

Figure 3.1 Localized surface plasmon resonance of metal particles

3.3. Fabrication

The first step of tunable color printing is manufacturing silicon mold with periodic subwavelength patterns. The manufacturing process is similar with the FIB nanofabrication method introduced in Chapter 2, but as the target material silicon's rigidity is much higher than silver, we should adjust the manufacturing condition as well. After trying different manufacturing conditions in FIB, beam current of 500 pA, dwelling time of 0.01 ms, 10000 times scanning was chosen to use. The size of 500 pA calcium ion beam is approximately 200 nm which is suitable for subwavelength manufacturing and the milling time is shorter than one hour when manufacturing the 600 nm periodic nanocavity structure within a 100 μm square area. The pattern design was also taken into consideration; in our experiment we designed two kinds of patterns: one is nanoholes with period of 600 nm in a 100 μm square area and one is nanoholes with different distances in a complicated pattern, and in all of them the nanohole diameter is 200 nm. The former pattern was designed to test micro-spectrum, and the later pattern was designed to show tunable color printing effect. Those patterned silicon wafers will be used as mold to transfer nanostructures from wafer to target nanocomposite material in the following steps.

The pattern transfer process was performed as showed in Fig.3.2. A shape mold was designed and manufactured by 3D printing, place the silicon wafer with the patterned face upward in the shape mold, and cast the liquid nanocomposite next. The subsequent gas extracting and solidifying process just perform the same steps as normal PDMS preparation. Place the sample in the constant temperature humidity chamber at 100℃ for 30 minutes, after curing finished, peel off the composite material from shape mold. In this way Ag-PDMS composite with periodic nanostructures on surface can be fabricated.

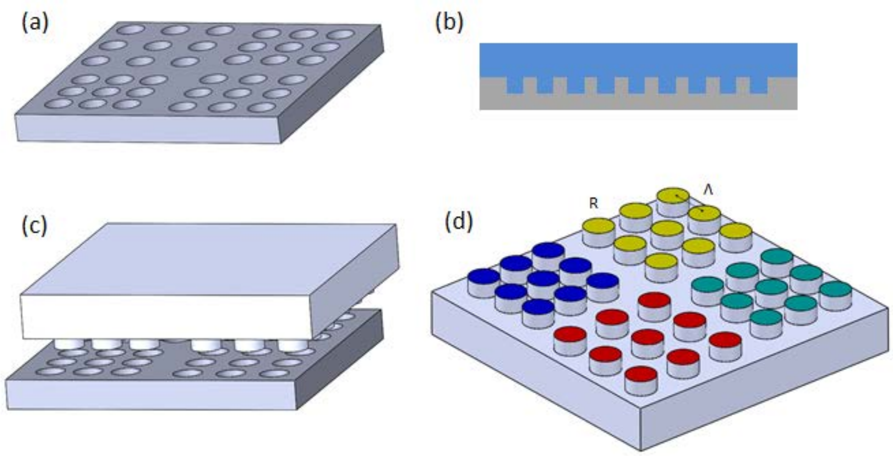

Figure 3.2 Color printing process on Ag-PDMS nanocomposite material. (a) Fabricate nanocavities on silicon wafer by FIB milling. (b) Cast uncured Ag-PDMS nanocomposite on silicon wafer mold. (c) Pell off nanocomposite material after curing finishing. (d) Structural color printed on material surface (R: pillar diameter, Λ: pillar distance).

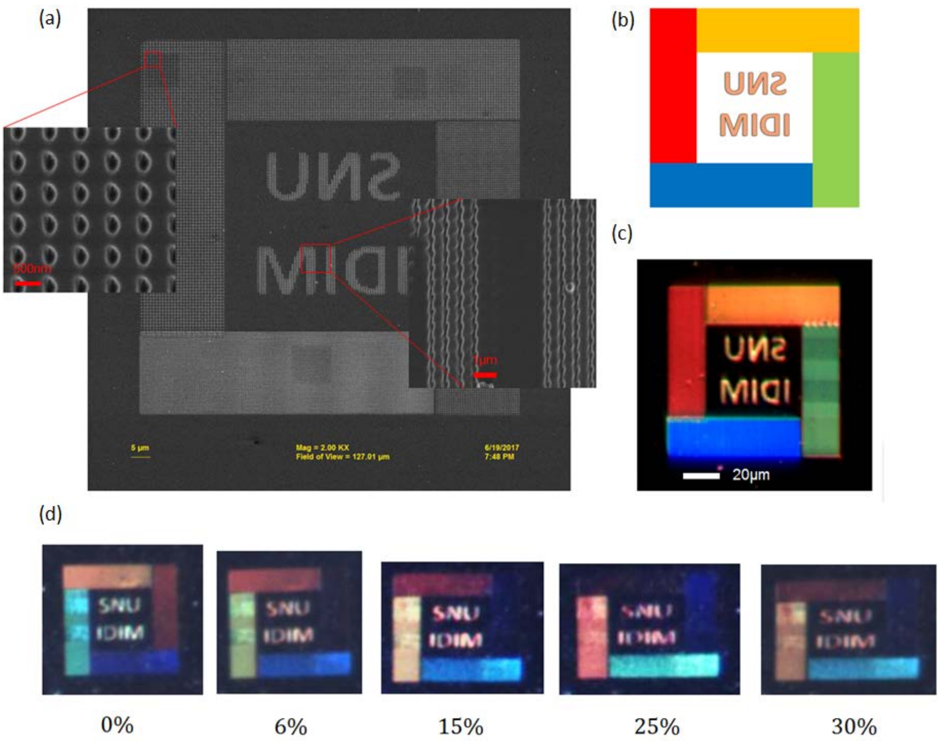

Figure 3.3 Silicon mold with 2D pattern: (a) FIB imagine; (b) original pattern; (c) microscope image; (d) Color shift of nanopillar structures on nanocomposite material with linear deformation.

3.4. Experiments

3.4.1. Active color tunability

By stretching the nanocomposite material with outer force, the distance and periodicity of nanostructures on the surface of material will change consequently. If the periodicity and geometry of plasmonic nanostructures changed, the surface plasmon resonance status will be different and the reflected plasmonic colors can be tuned actively in this way.

In order to show the color tunability of this nanocomposite material, we manufactured a color pattern composited of nanopillars with different distance as showed in Fig. 3.3. The experiment set is the same with the measurement system introduced in section 2.4, the illumination we use during the whole process is white light source with incident angle of 60° in the phase parallels with the horizontal direction of patterns.

The silicon mold in Fig 3.3 (a) was fabricated by the method introduced in section 3.3. At the surface of patterned silicon wafer, nanocavities with different periodicity show vivid iridescent colors under illumination. Casting from the silicon mold with nanocavities, on the surface of Ag-PDMS nanocomposite, nanopillar structures with inverse pattern can be manufactured. In Fig. 3.3 (d), we can observe that with the linear deformation of nanocomposite material, plasmonic color can be tuned continuously and precisely. The pattern shape maintains well and no cracking or breakage appeared during the stretching process. By adjusting the PDMS hardness in preparation process and thickness in casting process, the thickness and elasticity of this nanocomposite material can reach a linear deformation of 50% in our experiment, which is comparable with the latest elastomer optical materials [22].

3.4.2. Tunable color based strain sensor

Possessing the property of color changing with shape deformation, the Ag-PDMS nanocomposite with nanostructures on surface manufactured in our research can be used in strain sensor application. With the bending, twisting or linear deformation of this material, the periodicity of nanostructures on material can be changed simultaneously, and then different reflected plasmonic colors can be observed directly.

The traditional strain sensor is consisting of an insulating flexible backing which supports a metallic foil pattern, with the deformation of metallic foil, the electrical resistance will change as well, and then the strain change can be measured by the electrical signal change in the circuit [26]. Recently, with the development of functional material synthetic technology, new strain sensor mechanism has been developed such as disconnection between overlapped nanomaterials, crack propagation in thin films, and tunneling effect [27]. However, most of them cannot work independently without outer electric signal processing system, so the measurement method and working condition are limited. The tunable color based strain sensors introduced in our research, can be used to measure and monitor surface strain of any materials without additional device, the feedback color signal can be observed and evaluated directly by human eyes.

Soft robot is an emerging research filed in recent years which performs adaptation, sensitivity and agility when compared with the traditional rigid-bodied robots [28]. Composed of continuously deformable structure with muscle-like actuation, soft robots have a relatively large number of degrees of freedom. But one of the problems is that it is difficult to acquire the data of surface strain, bending angle that can be used to evaluate the motion state of soft robot. In this section we add nanostructure patterns on the surface of a shape memory composite (SMC) hinge, which is a basic and representative component of soft robot system. The color change with actuator deformation was tested and evaluated.

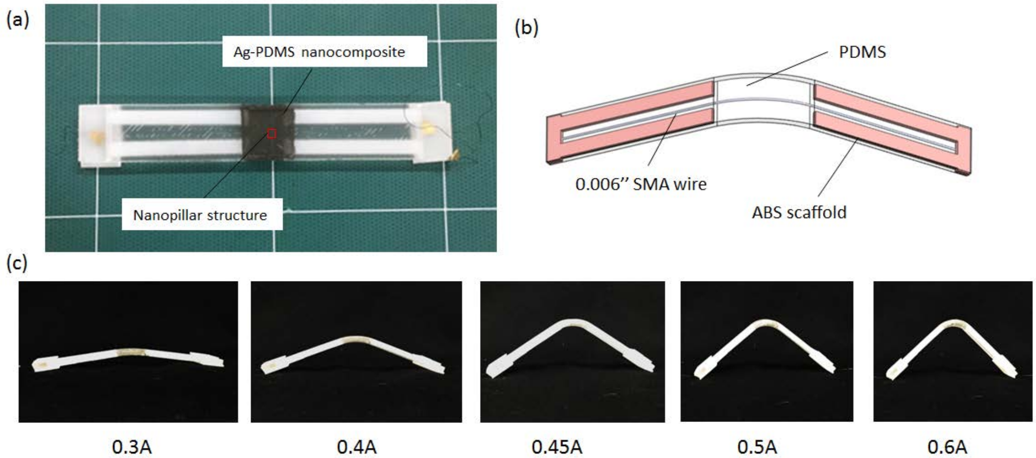

Figure 3.4 (a) SMC actuator with nanopillar structure on surface of hinge center. (b) SMC hinge actuator compoments (c) Actuator bending actuation by electric current heating.

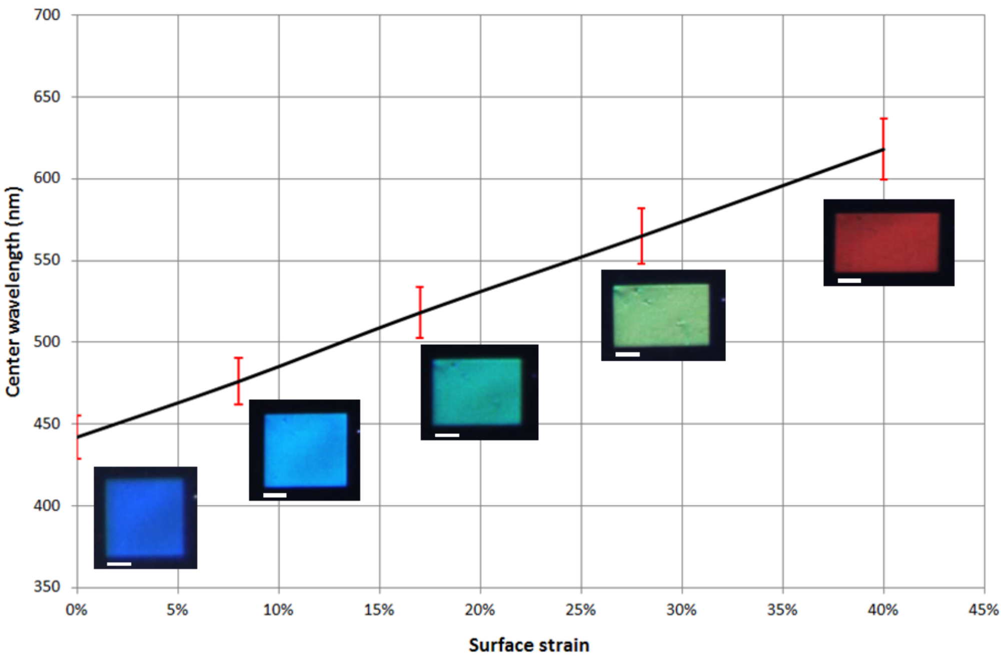

Figure 3.5 Relationship between surface strain and plasmonic colors. The scale bar is 30 μm.

The SMC actuator we use in this experiment was manufactured by following the design of Wang, W., et al [29] as shown in Fig. 3.4. This actuator was manufactured by embedding the pre-strained shape memory alloy (SMA) wire in a PDMS matrix eccentrically from neutral surface. The bending deformation was accomplished by the shape memory effect of the pre-strained SMA wire, which can return to its original shape when heating by electric currents. On the surface SMC actuator, we printed nanopillar structures in the area of 100x100μm square at the center of bending section with the same method introduced in section 3.3. The nanopillars' diameter is about 200nm, the periodicity of nanopillar structures is 600nm before bending deformation.

In order to observe color shift with shape deformation, we placed the SMC actuator with nanostructures under microscope, the color and spectrum test system is the same as in section 2.4. During the actuation test, the incident light was kept at the same incident angle of 60°. With the increase of electric current, the bending angle became larger and reached a maximum when the current was 0.6A. Under five different current conditions, we took microscope photos of surface nanopillar structures and measured the spectrum of reflected colors. Surface strain of SMC actuator can be calculated by the linear deformation of patterned squares. As shown in Fig 3.5, the reflected plasmonic color show color shifts form blue to red with the surface deformation increase, the center wavelength of plasmonic color and surface strain show approximately linear relationship. That's to say, without additional measurement tools, we can estimate surface strain just by the observed colors. The Ag-PDMS nanocomposite material with specific nanopattern, working as tunable color based strain sensor, can be pasted easily on other material which is necessary to test, and then the surface strain of target material can be measured and analyzed.

3.5. Summary

The tunable color printing process in our research was realized by replicating nanopatterns form silicon wafer to the surface of Ag-NPDS nanocomposite material. Different with previous stretchable nanostructure manufacturing method, we fabricate nanopillar structure with a single stretchable material instead of attaching nanostructures on a base material. The nanopillar structures were manufactured by casting the nanocomposite material on FIB nanofabricated silicon wafer. Based on the localized surface plasmon resonance of silver nanoparticles, the Ag-NPDS nanocomposite material performs excellent optical properties and can generate plasmonic colors with periodic nanostructures. At the same time, this material can be stretched with a large deformation up to 50% without any breakage or deformation, the periodicity of nanostructures on it can be tuned by the material deformation with a linear relation.

With the property of color changing with shape deformation, this tunable color printing technology can be used in stretchable color display or stain sensor application. As the tunable color based strain sensor introduced in our research, stretchable and wearable strain sensors are needed for several potential applications such as human motion detection, human-machine interfaces and soft robotics. Visualized color signal and flexible working environment will be the strengths of this tunable color based strain sensor compared with traditional sensors working with electric signals [30].

Chapter 4. Conclusion

The purpose of this research is to develop the tunable plasmonic color printing technology by focused ion beam nanofabrication. We explored passive tunable color printing process on metal thin film and active tunable color printing process on metal nanocomposite material.

To our knowledge, it was the first time manufacturing the reflective plasmonic color generated by FIB fabricated nanocavities on metal thin film. The plasmonic color printing process finished by FIB milling on silver thin film has a variety of advantages, such as short fabrication time, simple manufacturing process and pattern design flexibility. The target colors of printing can be tuned precisely by changing the FIB nanofabrication conditions, and vivid iridescence plasmonic colors have been printed with resolution up to subwavelength scale on the surface of silver film.

We also developed a new tunable color printing method by replicating nanopatterns from FIB patterned wafer to a kind of Ag-PDMS nanocomposite material. This composited can both serve as optical properties of silver and mechanical properties of PDMS. The periodicity of printed nanopillar structures can be changed with the deformation of material, therefore the reflective plasmonic color on material surface with those plasmonic structures also changed accordingly. The printed plasmonic color on Ag-PDMS nanocomposite material shows good color brightness and active color tunability by shape deformation.

The FIB fabrication, having advantages of high resolution, high flexibility rapid prototyping, is suitable for theoretical research and model test. If the plasmonic color printing process can be performed in larger area with faster process and lower cost, promising applications of color display and color related sensors are waiting to be explored.

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초록

플라즈모닉 컬러는 구조적 컬러로써 빛과 금속 나노구조의 상호공명에 의해 이뤄진다. 또한 프라즈모닉 컬러 구조의 제작 공정을 플라즈모닉 프린팅이라고 한다.

본 연구에서는 금속박막 및 금속 나노복합재료의 컬러 프린팅 공정에 대해 해석하였다. 첫번째로 금속박막 컬러 프린팅 구조는 집속이온빔 (focused ion beam) 밀링 공정을 이용하여 은 박막위에 일정한 패턴을 가진 나노캐비티를 가공하였다. 표면 플라즈몬 공명 원리에 따라 나노캐비티 거리를 조정하여 단일 은 박막위에 원하는 컬러를 프린팅 할 수 있다.

두번째 컬러 프린팅 구조를 제작하기 위해 집속이온빔을 이용한 실리콘 기판에 패턴을 가공한 후 나노 패턴을 은 나노입자와 폴리디메치실록산 (PDMS)를 1:100의 질량비로 혼합하여 제작한 신축성이 있는 광학 재료에 전사하여 제작하였다. 제작된 나노복합재료는 폴리디메치실록산의 양호한 신축성과 국소 표면 플라즈몬 공명 원리를 이용한 플라즈모닉 컬러 특성을 갖고 있다. 표면에 패턴을 가공한 유연한 나노복합재료는 스트레칭에 의해 나노 구조가 변형되며 따라서 재료 표면의 컬러가 변하게 된다. 형상기억복합재료 (shape memory composite) 구동기를 제작하여 구동기 표면에 본 연구의 방법으로 컬러 프린팅하며 색깔 변화를 이용한 스트레인 센서도 소개하였다.

넓은 범위의 컬러 변화가 가능하고 제작하기 편이한 장점을 이용하여 센서에 응용될 수 있으며 미래에는 플라즈모닉 컬리 디스플레이 기술에 적용될 수 있다.

주요어: 가변 플라즈모닉 컬러, 나노공정, 집속 이온빔, 나노 복합재료.

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